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ПОВЫШЕНИЕ ЭФФЕКТИВНОСТИ ПРОЦЕССА ТЕРМИЧЕСКОГО ПИРОЛИЗА

INCREASİNG THE EFFİCİENCY OF THE THERMAL PYROLYSİS PROCESS

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Аннотация. С ростом спроса на этилен и пропилен в промышленности, разведка новых сырьевых запасов и интенсификация процесса пиролиза стали важными вопросами из-за недостаточной доступности необходимого сырья для процесса пиролиза. Для этого была исследована эффективность процесса термического пиролиза путем добавления водорода и негидрированных фракций C_5 в различных соотношениях к процессу парового пиролиза для изучения их влияния на выход целевых продуктов. В ходе процесса поддерживалась температура в диапазоне 820–830 °C. Исследованиями установлено, что при соотношении однократной нафты к водороду 96,5:3,5 % по массе и соотношении сырьевой смеси к фракции C_5 (0–0,04): 1 % выход этилена снижается на 6,91 % по массе, а коксообразование снижается на 0,19 % по массе.

Ключевые слова: термический пиролиз, однократная нафта, бензол, толуол, кокс, фракция С5.

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Annotation. With the increasing demand for ethylene and propylene in the industry, the exploration of new raw material reserves and the intensification of the pyrolysis process have become important issues due to the insufficient availability of required raw materials for the pyrolysis process. For this purpose, the efficiency of the thermal pyrolysis process was investigated by adding hydrogen and non-hydrogenated C_5 fractions in various ratios to the steam-assisted pyrolysis process to study their impact on the yield of target products. During the process, the temperature was maintained within the range of 820–830 °C. The research determined that when the ratio of once-through naphtha to hydrogen is 96.5:3.5 % by mass and the ratio of the raw material mixture to the C_5 fraction is (0–0.04):1 %, the yield of ethylene decreases by 6.91 % by mass, while the coke formation decreases by 0.19 % by mass.

Keywords: thermal pyrolysis, once-through naphtha, benzene, toluene, coke, C5 fraction.

Introduction: In the global petrochemical industry, the pyrolysis process of hydrocarbon raw materials carried out in furnaces remains an irreplaceable process to this day. The raw material reserves and technological parameters of the process have practically remained unchanged [1, 2].

One of the solutions to this problem is the addition of hydrogen to the process during the pyrolysis of the initial gasoline fraction obtained from crude oil distillation for the production of lower olefins. At the same time, another approach involves adding the non-hydrogenated C5 fraction obtained from the pyrolysis process to once-through naphtha.

The purpose of this research was to study the effect of hydrogen-assisted pyrolysis of a mixture of initial distillation gasoline and non-hydrogenated C5 pyrolysis fraction on optimal technological parameters and the yield of target products.

As a result, it was determined that the pyrolysis of the initial distillation gasoline and non-hydrogenated C5 fraction mixture with the aid of hydrogen is feasible. Based on numerous studies, the mixture of once-through naphtha and non-hydrogenated C5 fraction in a 95.0:5.0 % ratio and the addition of hydrogen to the raw material in a (0.01–0.04): 1.0 % ratio were evaluated as the most optimal conditions for the pyrolysis process.

Experimentation:

For the laboratory experiments, the initial distillation gasoline used as raw material was obtained from the currently operating EÜDS-AVQ unit of the Heydar Aliyev Baku Oil Refinery. The non-hydrogenated C5 fraction for the pyrolysis process was sourced from the «EP-300» unit of the «Ethylene-Polyethylene» plant in Sumgait city. The physical and chemical properties of the raw material mixture are presented in Table 1.

During the experiments, standard methods were applied:

Density – ГОСТ 8.599-2010; Fraction composition – ГОСТ 2177-99; Actual resin content – ГОСТ 1567-97(ISO6246-95); Sulfur content-ГОСТ ISO 20846-2012; Hydrocarbon composition-Chromatogram «Net Chrom».

Table 1 – Physical and Chemical Properties of the Once-Through Naphtha and Non-Hydrogenated C_5 Pyrolysis Fraction Mixture

Indicators	* Regulatory Requirement	Once-Through Naphtha	Non-Hydrogenated C5 Pyrolysis Fraction
Appearance	Colorless transparent liquid	Colorless transparent liquid	Colorless transparent liquid
Density at 20 °C, g/m³	0,700–0.715	0,707	0,704
Molecular weight	–	95	69
Fractional composition, °C:			
– I.b.p.	45	42	33
– 10 %	68	63	35
– 50 %	105–110	96	38
– 90 %	165	137	58
– F.b.p.	170–180	165	62
Actual resin content, mg/100 cm³	0,5–2,0	none	16
Group composition, % mass:			
– n-paraffins	29,0	30,10	6,70
– isoparaffins	36,0	34,15	6,16
– naphthenes	30,0	29,56	3,55
– aromatic hydrocarbons	9,0	6,0	0,64
– unsaturated hydrocarbons	0,20	0,19	82,95
Sulfur content, % mass.	0,1	0,05	0,004

*-ТУ-0251-009-05766801-93. «Once-Through Naphtha».

The raw material mixture was prepared in a 95.0:5.0 % ratio of once-through naphtha to non-hydrogenated C_5 – pyrolysis fraction.

Table 2 – Hydrocarbon composition of the once-through naphtha and non-hydrogenated C_5 pyrolysis fraction mixture

Indicators	*Regulatory requirement	The mixture ratios of once-through naphtha and non-hydrogenated C_5 fraction.
		95,0:5,0 %
Appearance	Colorless transparent liquid	Colorless transparent liquid
Density at 20 °C, g/m³	0,700–0.715	0,707
Molecular weight	–	93
Fractional composition, 0C:		
– I.b.p.	45	40
– 10 %	68	59
– 50 %	105–110	90
– 90 %	165	138
– F.b.p.	170–180	165
Actual resin content, mg/100 cm³	0,5–2,0	3,0
Group composition, % mass:		
– n-paraffins	29,0	28,55
– isoparaffins	36,0	33,19
– naphthenes	30,0	27,35
– aromatic hydrocarbons	9,0	5,7
– unsaturated hydrocarbons	0,20	5,21
Sulfur content, % mass.	0,1	0,05

* ТУ-0251-009-05766801-93. «Once-Through Naphtha».

The principal scheme of the pyrolysis process set up in the laboratory conditions is shown in Figure 1. The pyrolysis study was conducted under conditions where a liquid hydrocarbon raw material mixture was involved with water steam and hydrogen. The pyrolysis of the prepared raw material mixture was carried out for 60 minutes, with the amount of raw material fed into the furnace being 150–160 cm³.

The ratio of water steam (Gw.s, %) to pyrolysis raw material (Gp.r, %) was calculated based on the molar quantity ratio of water steam (Nw.s) to pyrolysis raw material (Np.r) using the formula (1) [3, 4].

$$\frac{Gw.s}{Mw.s} : \frac{Gp.r}{Mp.r} = Nw.s : Np.r. \quad (1).$$

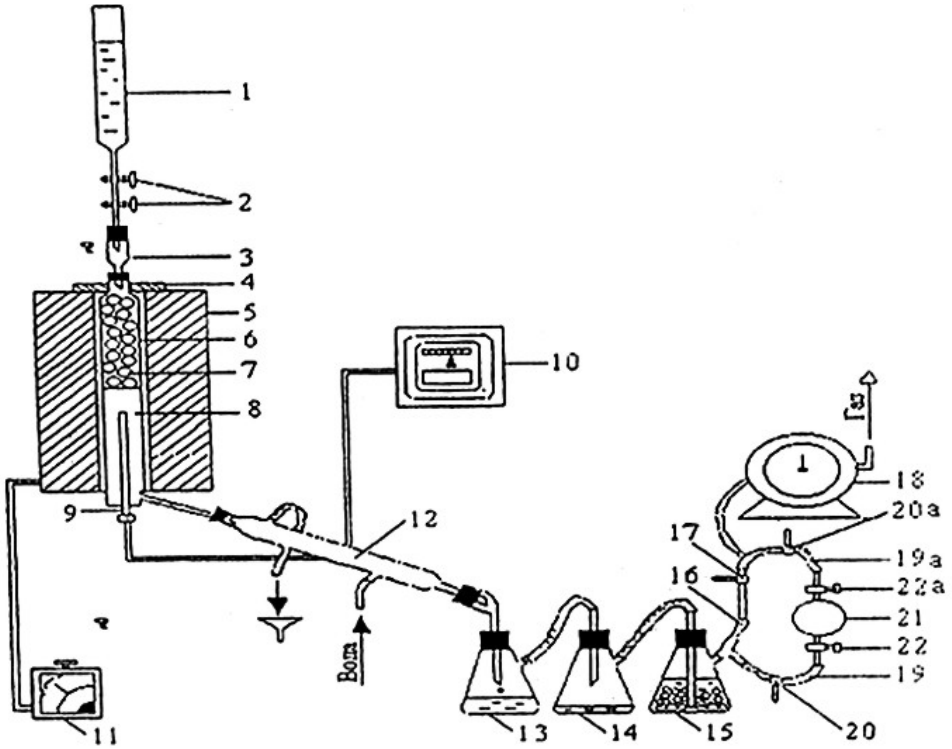

Figure 1 – Scheme of the laboratory installation of the process catalytic pyrolysis:
1 – raw burette; 2 – taps; 3 – allonge; 4 – lining; 5 – electric oven; 6 – reactor; 7 – nozzles; 8 – reaction zone; 9 – thermocouple; 10 – potentiometer; 11 – thermostat; 12 – refrigerator; 13 – receiving flask; 14 – flask intermediate; 15 – absorber; 16 – outlet of the gas meter; 17 – clamp medium; 18 – gas meter; 19 – gas inlet bypass; 19a – gas outlet bypass; 20 – terminal clamp; 21 – gas pycnometer; 22, 22 a – pycnometer tap

Experimental section:

Initially, once-through naphtha was subjected to pyrolysis with the participation of hydrogen in the temperature range of 820–830 °C. During this process, the contact time was set to 0.45 seconds, the ratio of water steam to raw material was 0.5:1.0 % by weight, and the ratio of hydrogen to raw material was (0–0.04):1.0 % by weight. After 10 minutes, the temperature of the process was increased from 820 °C to 830 °C. The selected conditions were fully aligned with the conditions of an industrial pyrolysis unit. The results of the experiment are presented in Table 3.

Table 3 – Pyrolysis of the once-through naphtha mixture with non-hydrogenated C_5 fraction in the presence of hydrogen (820 °C)

Mass ratio Hydrogen and raw material, %	0:1	0,02:1	0,03:1	0,04:1
1	2	3	4	5
The mixture of raw material with non-hydrogenated C_5 fraction	95,0:5,0 %			
Temperature	820 °C			
Hydrogen	0,90	2,00	2,51	3,06
Methane	9,42	11,16	12,08	12,20
Ethane	2,97	3,77	3,98	4,20
Ethylene	22,00	24,90	25,75	26,90
Acetylene	0,27	0,26	0,28	0,25
Propane	0,31	0,46	0,47	0,42
Propylene	15,70	15,60	14,88	14,20
MA-allen	0,41	0,36	0,33	0,34
∑ butane	0,88	0,83	0,71	0,67
∑ butylene	6,92	6,03	5,79	5,15

End of Table 3

1	2	3	4	5
Divinyl	5,00	4,48	4,23	4,03
∑ h/c C_5	9,43	7,86	7,65	7,17
∑ m, ar, h/c, C_6–C_8	11,03	8,57	7,82	7,33
Benzene	5,04	5,87	6,39	7,79
Toluene	2,59	2,46	2,29	2,12
∑ xylene	0,91	0,80	0,80	0,70
Ethylbenzene	0,38	0,39	0,34	0,20
Styrene	0,72	0,60	0,53	0,50
∑ m, ar, h/c, C_9	0,68	0,38	0,44	0,40
∑ ar, h/c, C_9	0,63	0,37	0,25	0,11
APQ	3,61	2,75	2,39	2,18
Coke	0,20	0,10	0,09	0,08
Total	100,00	100,00	100,00	100,00

When analyzing the experimental results presented in Table 3, it was determined that as the amount of hydrogen increased from 0 to 0.04 % by weight relative to the raw material at a temperature of 820 °C, the yield of gases increased, while the yield of liquid products decreased. Specifically, the yield of ethylene increased by 4.9 % by weight, hydrogen by 2.2 % by weight, methane by 3.4 % by weight, and ethane by 1.7 % by weight.

When the temperature of the process was raised from 820°C to 830°C, a decrease in the yield of propylene was observed, with hydrogen's ratio to the raw material being 0:1 % by weight, showing a reduction of 1.89 % by weight. Meanwhile, the yield of ethylene increased by 2.29 % by weight (Table 4).

Table 4 – Pyrolysis of the mixture of once-distilled gasoline and non-hydrogenated C_5 fraction with hydrogen participation at different ratios (830 °C)

Mass ratio Hydrogen and raw material, %	0:1	0,02:1	0,03:1	0,04:1
The mixture of raw material with non-hydrogenated C_5 fraction	95,0:5,0 %			
Temperature	830 °C			
Hydrogen	0,94	1,36	1,81	2,99
Methane	12,01	13,68	14,63	15,97
Ethane	2,70	3,43	3,95	4,48
Ethylene	24,29	26,58	27,49	28,91
Acetylene	0,32	0,40	0,42	0,49
Propane	0,31	0,31	0,35	0,39
Propylene	13,81	13,22	13,11	12,42
MA-allen	0,55	0,56	0,54	0,60
∑ buthane	0,52	0,50	0,40	0,38
∑ butylene	4,78	4,20	3,78	3,27
Divinyl	4,19	3,95	3,88	3,59
∑ h/c C_5	7,19	6,38	5,86	5,34
∑ m, ar, h/c, C_6–C_8	5,68	4,13	3,90	3,45
Benzene	7,93	8,57	8,79	8,97
Toluene	3,70	3,42	2,99	2,90
∑ xylene	1,00	0,90	0,90	0,64
Ethylbenzene	0,39	0,17	0,32	0,17
Styrene	1,35	1,20	0,96	0,74
∑ m, ar, h/c, C_9	0,38	0,46	0,24	0,10
∑ ar, h/c, C_9	0,32	0,24	0,13	0,04
APQ	7,31	6,12	5,37	4,02
coke	0,33	0.22	0,18	0,14
Total	100,0	100,0	100,0	100,0

The increase in process temperature and the corresponding increase in the hydrogen-to-feedstock ratio in the experiments lead to an increase in the ethylene yield from 22.00 % by mass to 28.91 % by mass. This shows a 6.91 % by mass increase in ethylene yield. At the same time, as seen in Tables 3 and 4, the formation of coke decreases by 0.12 % by mass at 820 °C and by 0.19 % by mass at 830 °C. These results enhance the efficiency of the pyrolysis process.

Conclusion: Based on the results of the experiments, it can be stated that the inclusion of various ratios of hydrogenated C5 fractions, obtained from the pyrolysis process itself, into the feedstock in the presence of hydrogen leads to an increase of 6.91 % by mass in the yield of the target product, which enhances the efficiency of the pyrolysis process. The optimal variant is when the hydrogen-to-feedstock ratio is 95.0:5.0 % by mass and the ratio of C_5 – fraction in the feedstock is 0.4:1 % by mass. The process was conducted with steam at a 0.5:1 % by mass ratio, and the contact time was 0.45 seconds. The increase in process efficiency under these conditions is due to the application of hydrogen in the pyrolysis of hydrocarbons, which accelerates the radical chain mechanism [5–8]. This occurs specifically with the participation of hydrogen. Additionally, the main radicals in the process, methyl and ethyl radicals, actively participate in the formation reactions of the chain and undergo substitution reactions with hydrogen atoms. The rate constant of the reaction of hydrogen with hydrocarbon molecules is higher compared to methyl and ethyl radicals. As the temperature increases, hydrogen fully participates in the decomposition of hydrocarbons. This can be explained by the increased reactivity of hydrogen atoms at high temperatures.

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